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(54) Title: POWDER COATING COMPOSITIONS AND A METHOD FOR COATING A SUBSTRATE			
(57) Abstract			
<p>A powder coating composition comprising a powdered solid ethylenically unsaturated material having a melting point from 60° to 120 °C obtained by reacting a polyisocyanate with an at least stoichiometric amount of an alcoholic component comprising: at least a monovalent alcohol, a part of which bears an ethylenic unsaturation derived from acrylic acid or methacrylic acid, and optionally at least a monomeric polyol. This composition is used for coating substrates.</p>			

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## POWDER COATING COMPOSITIONS AND A METHOD FOR COATING A SUBSTRATE.

This invention is concerned with improvements relating to powder coating compositions and methods of coating substrates 5 using such compositions.

- Powder coating is a well-established process, basically comprising the application of a powdered fusible material to a substrate, heating of the powder in contact with the substrate to cause the powder to melt and reflow, and cooling the resultant melt 10 to form a solid coating on the substrate. The coating material may simply comprise a film-forming thermoplastic material or may comprise a reactive material, e.g. an epoxy resin together with a curing agent therefore, so that during the course of melting and reflowing reaction occurs to cure the material in situ on the 15 substrate. In any event, powder coating materials are generally such that they have to be melted and reflowed at relatively high temperatures, e.g. 150°C or more. As a result, powder coating processes are generally not suitable for the coating of heat-sensitive materials such as wood or plastics material. In order to coat such 20 materials, it would be necessary to have a product which had a relatively low melting temperature, e.g. below about 120°C, whilst at the same time being solid at ambient temperature, which material could subsequently be cured in situ on the substrate during the melting/reflowing stage or, afterwards.
- 25 U.S.-A-4 093 674 discloses a thermosetting powder coating composition comprising a solid resin having a Tg from 5° to 150°C and free hydroxyl groups and a solid polyisocyanate compound, with a molar ratio of isocyanate groups in the latter to active hydrogen in the former of 0.2 to 2. Among examples of the solid resin are the 30 polymers of hydroxyalkylacrylates preferably with Mn from 1 000 to 30 000. This powder coating composition is said to provide advantages over isocyanate crosslinking-type urethane resins wherein all the isocyanate groups are previously blocked with a phenol or an alcohol.
- 35 G.B.-A-1 590 413 discloses a urethane resin having at least 2 terminal ethylenically unsaturated groups and comprising the

reaction product of at least one isocyanate-functional prepolymer and at least one unsaturated monomer having a single isocyanate-reactive-hydrogen-containing group, said isocyanate-functional prepolymer being the reaction product of (i) at least one diisocyanate and (ii) a mixture of at least 2 polyols (at least 30 mole % being polymeric and at most 70 mole % being monomeric in the said mixture) in an NCO : OH ratio of at least 2.3. This urethane resin is mixed with similar unsaturated materials derived from polymeric polyols, with the unreacted excess of diisocyanate and with a reactive diluent which at the end produces flowable and fluid compositions with viscosities of about 4.5 Pa.s. No mention of powder coating may be found in this document.

U.S.-A-4 500 696 discloses powder surface coatings comprising polyols and a polyisocyanate component comprising blocked adducts of aliphatic diisocyanates. They involve no unsaturated alcohol.

U.S.-A-5 089 586 discloses acrylate-free water-dispersible allyl urethanes prepared from a polyglycol or its reaction product with an unsaturated dicarboxylic acid, a hydroxyallyl compound (preferably an allyl ether) and a diisocyanate.

International Application WO-93/19132 discloses mixtures, in a binder composition for powder coatings, of an unsaturated polyester and an oligomer having a plurality of allyl ether groups and having further urethane groups.

It has now been found, in accordance with the present invention, that useful solid ethylenically unsaturated materials, having relatively low melting point and suitable for use in powder coating compositions may be prepared by reacting a diisocyanate with one or more monohydric alcohols, optionally in combination with a dihydric alcohol.

According to one embodiment of the invention, therefore, there is provided a powder coating composition comprising a powdered solid ethylenically unsaturated material having a melting point from about 60° to 120°C obtained by reacting a polyisocyanate with an at least stoichiometric amount of an alcoholic component comprising :

- at least a monovalent alcohol, a part of which bears an ethylenic unsaturation derived from acrylic acid or methacrylic acid, and optionally
- at least a monomeric polyol.

5 In accordance with a preferred embodiment of the invention the polyisocyanate is reacted with an at least stoichiometric amount of :

- (i) a monohydric alcohol component, or
- (ii) a monohydric alcohol component followed by another different monohydric alcohol component, or
- 10 (iii) a monohydric alcohol component, followed by a dihydric alcohol component, followed by a monohydric alcohol component, or
- (iv) a dihydric alcohol component, followed by a monohydric alcohol component alone or in admixture with a dihydric alcohol component,

15 the monohydric alcohol component(s) comprising a monohydric aliphatic alcohol or an etherified or esterified dihydric aliphatic alcohol or dihydric polyalkylene glycol, at least a part of which bearing an ethylenic unsaturation derived from acrylic acid or methacrylic acid and the dihydric alcohol component comprising a dihydric aliphatic alcohol or a dihydric polyalkylene glycol and being preferably used in an amount not more than about 50%, preferably not more than 25%, of the stoichiometric amount of hydroxyl groups required to react with the isocyanate groups on the polyisocyanate.

20 As noted above, it is a requirement of the present invention that the material obtained (hereinafter simply referred to as an "oligourethane", "urethane acrylate" or "oligomer") have a melting point of from about 60 to 120°C (the term "melting point" as used herein means the melting point as determined by the ring and ball method).

25 It is also most often preferred that the powdered solid material of the invention have a viscosity in the range from about 0.1 Pa.s to about 2.5 Pa.s.

30 35 Suitable polyisocyanates for use in the preparation of the oligourethanes include toluene diisocyanate, diphenylmethane-4,4'-

diisocyanate, hexamethylene-1,6-diisocyanate, naphylene-1,5-diisocyanate, 3,3'-dimethoxy-4,4'-biphenyldiisocyanate, 3,3'-dimethyl-4,4'-biphenyldiisocyanate, phenylene diisocyanate, 4,4'-biphenyldiisocyanate, isophorone diisocyanate, trimethylhexamethylene diisocyanate and tetramethylene xylene diisocyanate.

A wide variety of monohydric aliphatic alcohols may be used to produce the oligourethanes, e.g. C<sub>1</sub> to C<sub>22</sub> alcohols. Typical etherified dihydric alcoholic materials which may be used as monohydric alcoholic component include propylene glycol methyl ether, 10 dipropylene glycol methyl ether, ethylene glycol butyl ether, diethylene glycol butyl ether, tripropylene glycol butyl ether and propylene glycol phenyl ether. Dihydric alcohols which may be used include, for example, saturated aliphatic diols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 15 dipropylene glycol, tripropylene glycol, butylene glycols, neopentyl glycol, 1,3- and 1,4-butane diols, 1,5-pentane diol, 1,6-hexanediol, 2-methyl-1,3 propanediol, glycerol, and 1,1,1-trimethylolpropane.

The reaction between the polyisocyanate and the monohydric/dihydric alcohol component is suitably carried out in 20 the presence of a catalyst. As such a catalyst the following may be mentioned :

- (a) tertiary amines such as bis(dimethyl amino ethyl)ether, trimethyl amine, triethyl amine, N-methyl morpholine, N-ethyl morpholine, N,N-dimethyl benzylamine, N,N-dimethyl ethanol amine, N,N,N',N'-tetramethyl-1,3-butane diamine, triethylanol amine, 1,4-diazabicyclo(2.2.2.)octane and pyridine oxide,
- (b) tertiary phosphines such as trialkyl phosphines and dialkyl benzyl phosphines,
- (c) strong bases such as the hydroxides, alcoholates and phenolates of alkali metals and alkaline earth metals,
- (d) metal salts of strong acids such as ferric chloride, stannic chloride and bismuth chloride, antimony trichloride and bismuth nitrate,
- (e) chelates, such as those which can be obtained from acetyl acetone, benzoyl acetone, trifluoroacetyl acetone, ethyl acetoacetate, salicylaldehyde, cyclopentanone-2-carboxylate,

- acetyl acetoimine, bis-acetyl acetone alkylene diimines, salicylaldehyde imine, and from metals such as beryllium, magnesium, zinc, cadmium, lead, titanium, zirconium, tin, arsenic, bismuth, chromium, molybdenum, manganese, iron, cobalt and nickel,
- 5 (f) alcoholates and phenolates of metals, such as  $Ti(OR)_4$ ,  $Sn(OR)_4$ ,  $Sn(OR)_2$  and  $Al(OR)_3$ , in which R is an alkyl or aryl group.
- (g) the salts of organic acids and of metals, such as alkali metals and alkaline earth metals, aluminium, tin, lead, manganese, cobalt, nickel and copper, for example sodium acetate, potassium laurate, calcium hexanoate, stannous acetate, stannous octoate and stannous oleate, lead octoate, manganese and cobalt napthenates, and
- 10 15 (h) iron and cobalt metal carbonyls and organometallic derivatives of tetravalent tin, of trivalent and pentavalent arsenic, of antimony and of bismuth; particularly preferred are the salts of dialkyl tin carboxylic acids, such as dibutyl tin diacetate, dibutyl tin dilaurate, dibutyl tin maleate, dilauryl tin diacetate, dioctyl tin diacetate, dibutyl tin bis(4-methylamino benzoate), dibutyl tin bis(6-methylamino caproate), trialkyl tin hydroxides, dialkyl tin oxides, dialkyl tin dialcoxides and dialkyl tin dichlorides.
- 20 Said catalyst is generally used at a rate of from about 0,01 to about 2% by weight of the polyisocyanate.
- 25 The molecular weight of the final oligourethane is suitably from about 500 to about 3 000, preferably from about 500 to about 1 500.
- For some applications it is desirable that the oligourethanes be clear. It is not possible to predict whether any particular
- 30 oligourethane produced in accordance with the invention will, or will not, have the desired optical properties in this respect. However, here again it is a matter of simple routine trial and experiment.
- The ethylenically unsaturated solid material forming a part of
- 35 the powder coating composition in accordance with the invention is in powdered form, e.g. has an average particle size from about 10 to

about 250 µm, especially from 10 to about 90 µm. In addition to the particulate, ethylenically unsaturated material, a powder coating composition in accordance with the invention preferably further comprises a curing system for the ethylenically unsaturated material.

5       In accordance with one embodiment of the invention, the curing system may comprise a thermally initiated peroxide or like free radical-generating catalyst, optionally together with one or more promoters therefore. Suitable examples of such free radical-generating catalysts include 1,1-bis(*t*-butylperoxy)-3,5,5-trimethyl 10 cyclohexane, 1,1-bis(*t*-butylperoxy)-cyclohexane, *t*-butylperoxy-isopropyl carbonate, *t*-butyl perisononanoate, *t*-butyl peracetate, *t*-butyl perbenzoate, dicumyl peroxide, di-*t*-butyl peroxide, *t*-butyl hydroperoxide, *t*-butyl perneodecanoate, diisooctanoyl peroxide, dibenzoyl peroxide, and azo bis (isobutyronitrile).

15      Preferably, the catalyst system is selected so that the powder can melt and reflow prior to curing. This makes it possible to obtain a level film, in contrast to conventional epoxy/acid powders in which curing is effected during melting and reflowing, leading to an organo peel effect.

20      In accordance with another embodiment of the invention, the curing system may further comprise one or more photoinitiators, sensitive to ultraviolet light, optionally together with sensitizers therefore. By operating with such a system, the coating composition may be allowed to cool and solidify after melting/reflowing and then 25 be subjected to appropriate irradiation to cure the coating.

          Examples of suitable photoinitiators include benzylidemethyl ketal, trimethylbenzophenone, isopropylthioxanthone, ethyl 4-dimethylamino benzoate, benzophenone, 2-chloro- and 2-ethyl-thioxanthone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxy-30 acetophenone, 2-hydroxy-2-methyl-1-phenyl-prepanone, 4-benzoyl-4'-methyl-diphenyl sulphide, 1-hydroxycyclohexyl-acetophenone, and 2-ethyl-hydroquinone.

          Examples of suitable sensitizers include 4,4-dimethylamino-benzophenone, triethanolamine, N-methyl-diethanolamine, 2-35 (butoxy)ethyl, 4-dimethylamino benzoate and acrylated amines.

In accordance with another embodiment of the invention, the curing system may be absent and curing of the solidified coating on the substrate may be effected by electron beam.

In addition to the basic components noted above, powder 5 coating compositions in accordance with the invention may, and often do, contain other ingredients particularly colorants such as pigments or dyestuffs. Other components which may be present include flow aids, anti-cissing agents, flexibilizers, degassing agents and inorganic fillers.

10 The invention also provides a powder coating process for coating a substrate which comprises applying a powder coating composition in accordance with the invention to the substrate, heating the composition to melt and reflow it on the substrate, and allowing the composition to cool on the substrate. In the case of the 15 first embodiment of the invention discussed above, curing of the coating will preferably be effected by free radical polymerisation after the melting/reflowing step, whereas in the second embodiment of the invention an additional curing step is required, that is the substrate bearing the cured coating must be subjected to 20 ultraviolet or electron beam radiation.

In order that the invention may be well understood the following examples are given by way of illustration only. Unless stated otherwise, all amounts are expressed by weight.

EXAMPLE 1

25 500 g of isophorone diisocyanate and 0.2 g of hydroquinone were charged to a 1 litre round bottomed flask which was fitted with a stirrer, thermometer, air sparge and an addition funnel. Heat was applied and the temperature was raised to 90°C with continued air sparging at a rate 1.51/hour. Upon reaching 90°C a mixture of 286 g 30 of hydroxyethyl methacrylate and 10.5 g of hydroxyethyl acrylate was added to the contents over 1 hour. The temperature was then raised to 100°C and the isocyanate value was monitored until it falls below 165 mgKOH/g which should usually take about 2 hours. Then 117.6 g of neopentyl glycol was charged and the temperature was raised to 35 115°C, the temperature was maintained at 115°C with the air sparge at 1.51/hour until the isocyanate value fell below 30 mgKOH/g and

then 0.3 g stannous octoate was added. The urethane will then exotherm to about 135°C and should be cooled back to 120°C at which temperature it is maintained until the NCO value falls to less than 30 ppm. The urethane acrylate was then discharged and 5 allowed to cool. The material produced is a transparent, clear, tack free solid with a melting point of 77°C (ring and ball method) and a viscosity of 0.55 Pa.s at 125°C (REL cone & plate viscometer). This material was called Resin A.

10 The following formulation was then mixed in a heated screw extruder using a screw speed of 250 rpm to give a dwell time of the product in the extruder of 5 seconds. The product temperature was kept between 105° and 110°C with the wall temperature being maintained at 125 - 130°C.

Resin A	96.0
15 Flow Aid (Modaflo 2 marketed by MONSANTO)	3.8
2,2'-Azobisisobutyronitrile (WAKO CHEMICALS GmbH)	0.2

20 This solid was then ground and classified to give a particle size of less than 90 µm and then sprayed onto a mild steel panel giving a film thickness of 15 µm. The panel was then placed in a fan assisted oven for 10 minutes at 100°C and then allowed to cool. Once cool the panel was seen to produce a perfectly levelled film with excellent adhesion, hardness and solvent resistance.

EXAMPLE 2

25 250 g of diphenyl methane-4,4'-diisocyanate and 0.1 g of dibutyl tin dilaurate were charged to a 1 litre round bottomed flask fitted with a thermometer, air sparge and an addition funnel. The contents were heated to 45°C and 37 g of dipropylene glycol methylether were added and the temperature allowed to rise to 30 60°C. Then 67.5 g of octadecanol was charged and the temperature raised to 110°C, at which temperature 0.5 g of hydroquinone was added. An air sparge was set at 1.5 l/hour and bubbled through the material while 116 g of hydroxyethyl acrylate was added over 1 hour while maintaining the batch temperature at 110°C until the isocyanate value falls below 30 mgKOH/g. Then 33.5 g of dipropylene 35 glycol was charged and the batch temperature raised to 120°C and held until the NCO value is lower than 30 ppm. The urethane

acrylate was then discharged and allowed to cool. It was found that the material produced was a very hard solid with a melting point of 101°C and had a extremely low viscosity of only 0.1 Pa.s at 125°C. This material is called Resin B.

5       Resin B was extruded with 0.5% of a thermal initiator benzoyl peroxide and 2% of Modaflo, at a screw speed of 200 rpm giving a residence time in the extruder of about 10 seconds. The temperature was maintained between 110 and 115°C with the wall temperature between 120 and 125°C. The final product has a gel 10 time of 3.5 minutes at 110°C. The resultant material was then ground and classified to less than 90 µm and electrostatically applied to a chromated aluminium test panel. The panel was then reflowed and cured in a fan assisted oven at 120°C for 10 minutes to yield a film with a Koenig hardness of 80% and a methyl ethyl ketone swab 15 resistance of more than 200 rubs.

EXAMPLE 3

20      421.4 g of isophorone diisocyanate and 0.15 g of Ethanox 703 (ETHYL SA) were charged to a 1 litre round bottomed flask which was fitted with a stirrer, thermometer, nitrogen sparge and an addition funnel. The contents were then heated to 70°C, the nitrogen sparge set at a flow rate of 1.51/hour and 148.1 g of hydroxyethyl acrylate and 133.5 g neopentyl glycol added. The batch was then reheated to 70°C and allowed to exotherm to 125°C at which temperature it was maintained at. The isocyanate value was 25 then monitored until it falls to less than 15 mgKOH/g and 0.3 g of stannous octoate added. The temperature was then raised to 130°C and held until the isocyanate value falls to less than 30 ppm and then discharged and allowed to cool. A clear material was obtained that had a viscosity of 0.24 Pa.s (Rel 150°C cone & plate) and a melting 30 point of 103°C. This product was called Resin C.

Resin C was then extruded in the following formulation :

Resin C	91.0
Quantacure ITX (WARD BLENKINSOP)	2.0
Irgacure 907 (CIBA GEIGY)	3.0
35   P104 sensitizer (UCB)	2.0
Modaflo	2.0

The screw speed of the extruder was set at 250 rpm, batch temperature between 125 and 130°C and wall temperature between 140 and 145°C providing a residence time in the extruder of about 7 seconds. The solid product produced was then kibbled and ground

5 in a coffee grinder to give a fine powder. This was then sieved to a particle size of less than 90 µm. A 15 x 10 cm glass panel was then moistened with an aqueous surfactant solution and the above powder applied to a film thickness of 40 µm. This was then fully cured by exposure to ultraviolet light giving a film with a Koenig hardness

10 80% and a solvent resistance of more than 200 methyl ethyl ketone rubs.

EXAMPLE 4

348 g of toluene diisocyanate, 232 g of hydroxyethyl acrylate, 122 g 1,6-hexane diol and 0.2 g Ethanox 703 were charged to a

15 round bottomed flask fitted with a stirrer, thermometer and a nitrogen sparge. The nitrogen sparge was set at 1.51/hour and the temperature was allowed to rise from 20°C to 120°C without the application of heat. When the temperature reached 120°C heat was applied to maintain the temperature at this level and the isocyanate

20 value was monitored until it fell below 30 ppm. The batch was then discharged and allowed to cool. A slightly coloured, clear product was obtained with a viscosity of 0.47 Pa.s (Rel 125°C cone & plate) and a melting point of 64°C. This product was called Resin D.

500 g of Resin D was reheated to 120°C and mixed with 15 g

25 benzophenone, 10 g CN 381 (an acrylated amine synergist marketed by SARTOMER Company) and 5 g Modaflow. The material was then held at 120°C for 30 minutes and then discharged and allowed to cool. The product was kibbled and ground up into a fine powder using a coffee grinder. It was then sieved and ground through a

30 90 µm test sieve before being electrostatically sprayed onto a chromated aluminium test panel to a film thickness of 25 µm. The test panel was then put in a fan assisted oven for 10 minutes at 95°C to reflow the powder, the panel was then removed from the oven giving a blemish free perfectly levelled film. The panel was then fully

35 cured by exposure to ultraviolet light in a SPECTRAL Minicure unit giving the following test results :

Koenig Hardness	75%
Adhesion (x-hatch)	100%
Reverse Impact	127 cm/454 g Pass
	64 cm/454 g Pass
5 Conical Bend	Pass
Methyl ethyl ketone Resistance	> 200 rubs

EXAMPLE 5

392.3 g of toluene diisocyanate, 178.4 g of hydroxyethyl acrylate, 159.5 g neopentyl glycol and 0.2 g Ethanox 703 were charged to a round bottomed flask fitted with a stirrer, thermometer and a nitrogen sparge. The nitrogen sparge was set at 1.5 l/hour and the temperature was allowed to rise from 20°C to 135°C without the application of heat. When the temperature reaches 135°C heat was applied to maintain the temperature and the isocyanate value was monitored until it fell to below 30 ppm. The batch was then discharged and allowed to cool. A slightly coloured, clear product was obtained with a viscosity of 0.84 Pa.s (Rel 175°C cone & plate) and a melting point of 112°C. This product was called Resin E.

Resin E was then extruded in the following formulation :

20	Resin E	93.0
	Flow Aid (Modaflo)	2.0
	N-methyldiethanolamine (BASF)	2.0
	Lucirin TPO (BASF)	3.0

The screw speed of the extruder was set at 250 rpm to give a residence time in the extruder of 89 seconds. The product temperature was kept between 130 and 135°C with the wall temperature maintained between 150 and 155°C. The solid product produced was then ground and classified to a particle size of 90 µm. The final powder had very good stability showing no cold flow at temperatures of up to 40°C.

A sapele veneered medium density fibre - board 19 cm x 29 cm x 0.5 cm was lightly damped with water and sprayed with the above formulation to a film thickness of 30 µm. The substrate was then placed in a oven for 10 minutes at 125°C to yield a completely levelled tack free film. The substrate was then twice passed through a SPECTRAL Minicure unit with a belt speed of

5 m/min. to raise the methyl ethyl ketone resistance from 3 rubs to more than 200 rubs. The final film produced was then evaluated as follows :

	Impact Test	BS3962 Part 6	4
5	Cross Hatch	BS3962 Part 6	4
	Wet Heat	BS3962 Part 2	55°C 5
			70°C 5
			85°C 5
	Dry Heat	BS3962 Part 3	85°C 5
10			100°C 5
			120°C 5
			140°C 5
			160°C 5
	Marking by Liquids	BS3962 Part 4	Acetone 5
15			Butyl Acetate 5
			Toilet Spirits <sup>1</sup> 5
			Potable Spirits <sup>2</sup> 5
			Tea 5
			Coffee 5
20	Koenig Hardness		80%
	Methyl ethyl ketone swabs		> 200
	Xylene swabs		> 200
	60% Gloss	Along Grain	95%
		Against Grain	95%
25	Scrape Test	BS3962 Part 6	4
	<sup>1</sup> 8:1 industrial methanol : water mixture		
	<sup>2</sup> 1:1 industrial methanol : water mixture		
30	The system passes BS6250 general and severe ratings exhibiting extremely good hardness and resistance properties. The heat resistance is also extremely good. It also passes DIN 68861 group A (chemical resistance and stain tests).		

CLAIMS

1. A powder coating composition comprising a powdered solid ethylenically unsaturated material having a melting point from 60° to 5 120°C obtained by reacting a polyisocyanate with an at least stoichiometric amount of an alcoholic component comprising :
  - at least a monovalent alcohol, a part of which bears an ethylenic unsaturation derived from acrylic acid or methacrylic acid, and optionally
  - 10 - at least a monomeric polyol.
2. A powder coating composition according to claim 1, characterized in that the monomeric polyol is a dihydric aliphatic alcohol or a dihydric polyalkylene glycol.
3. A powder coating composition according to claim 2, 15 characterized in that the said dihydric aliphatic alcohol or dihydric polyalkylene glycol is used in an amount not more than 50% of the stoichiometric amount of hydroxyl groups required to react with the isocyanate groups of the polyisocyanate.
4. A powder coating composition according to any of claims 1 to 20 3, characterized in that the powdered solid material has a viscosity in the range from 0.1 Pa.s to 2.5 Pa.s.
5. A powder coating composition according to any of claims 1 to 4, characterized in that the reaction of the polyisocyanate with the alcoholic component is carried out in the presence of a catalyst 25 selected from tertiary amines, tertiary phosphines, strong bases, metal salts of strong acids, chelates, metal alcoholates and phenolates, organic metal salts, iron and cobalt carbonyls, and organometallic derivatives of tin, arsenic, antimony and bismuth.
6. A powder coating composition according to any of claims 1 to 30 5, characterized in that the molecular weight of the solid ethylenically unsaturated material is from 500 to 3 000.
7. A powder coating composition according to any of claims 1 to 6, characterized in that the solid ethylenically unsaturated material has an average particle size from 10 to 250 µm.

8. A powder coating composition according to any of claims 1 to 7, characterized in that it further comprises a curing system for the ethylenically unsaturated material.
9. A powder coating composition according to claim 8,  
5 characterized in that the curing system comprises a thermally initiated free-radical generating catalyst.
10. A powder coating composition according to claim 8, characterized in that the curing system comprises a photoinitiator sensitive to ultraviolet light.
- 10 11. A powder coating composition according to claim 10, characterized in that the curing system further comprises a sensitizer.
12. A powder coating composition according to any of claims 1 to 11, characterized in that it further comprises at least one other  
15 ingredient selected from pigments, dyestuffs, flow aids and inorganic fillers.
13. A method of coating a substrate which comprises applying a coating composition according to any of claims 1 to 12 to the substrate, heating the composition to melt and reflow it on the  
20 substrate, and allowing the composition to cool on the substrate.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 95/02332A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08F20/36 C08G18/67 C09D175/16 C09D4/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08F C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 410 242 (BAYER) 30 January 1991 see claim 1 see page 2, line 18 - page 3, line 32 ---	1-13
X	FR,A,2 091 106 (WITCO CHEMICAL CORP.) 14 January 1972 see claims 1,6-11 see page 1, line 22 - page 2, line 8 see page 26, line 17 - line 34 ---	1,5,8-13
A	US,A,4 078 015 (R.H. LEITHEISER ET AL.) 7 March 1978 see claims 1,2,10,11 see column 1, line 29 - line 39 ---	1 -/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

Inten. nal Application No  
PCT/EP 95/02332

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,1 443 715 (KANSAI PAINT CO.) 21 July 1976 see claims 1-22,34,66-72 see page 5, line 8 - page 6, line 46 see page 8, line 5 - line 56 see page 10, line 7 - line 28 ----	1
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